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XI.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE. — J. P. Cooke, *Director.*

FURTHER INVESTIGATION ON THE ATOMIC WEIGHT OF COPPER.

By Theodore William Richards.

Presented by J. P. Cooke, June 15, 1887.

In the last volume of these Proceedings there appeared a description of a new determination of the atomic weight of copper, based upon the precipitation of silver from a neutral solution of argentic nitrate by pure metallic copper. In the course of some further experiments, it became necessary to ignite a portion of the silver from determination No. 5 of that series; and it was found that two grams of silver lost four tenths of a milligram by this process. It is thus evident that 150° is not a temperature high enough to drive out all the water from the silver, and hence the results before given are incorrect by a slight amount. In this determination the weight of the silver was 3.39035 grams, after drying at 150°, hence its weight after ignition would have been 3.38975 grams. The weight of copper taken was .9987 grams, therefore the corrected atomic weight of copper would be 63.452, instead of 63.437.

Unfortunately, all the silver formed in the other determinations had been employed in testing for the presence of copper; hence it was impossible to determine whether the other samples would lose water on heating in a similar manner. It seemed, therefore, desirable to make a new series, using samples of pure copper, prepared from the ores of different localities. Should the result be the same in each instance, we should have a very strong proof, not only that the copper used in each case was pure, — because the different samples would probably contain different impurities, — but also that the atomic weight of copper is a perfectly constant quantity.

The method used was exactly that of the previous paper, although more difficulty was found in keeping the solution below zero for twenty-four hours than was the case before, because of the warmer weather. Several determinations had to be rejected because the temperature rose above zero, and copper was precipitated with the silver. Upon splitting open the fine crystalline plates of silver precipitated in these rejected experiments, a light green precipitate of basic cupric nitrate was found adhering to the inner surface, which could not be removed by continued washing with cold water. The presence of this precipitate explains the admixture of copper with the silver precipitated above zero, and points at once to the mechanism of the chemical action.

When copper is placed in a solution of argentic nitrate, two reactions take place, and the temperature regulates the predominance of one or the other. The chief reaction is the simple one ordinarily written; it alone is active between 0° and —5°, and it is the chief one even at 100°. The secondary reaction, which is active at 100°, but which entirely ceases below 0°, may perhaps be written thus, — assuming that the basic nitrate has the formula usually assigned to it: —

$$4\,AgNO_3 + 4\,Cu + 3\,H_2O = Cu(NO_3)_2 \cdot 3\,Cu(OH)_2 + 2\,Ag_2 + NO + NO_2.$$

Evidently in this reaction the copper precipitates only one half of its equivalent of silver. It will be remembered that an evolution of nitrous fumes was previously observed, when the temperature rose above the freezing point.

The argentic nitrate used in the new series was prepared as before, except that even greater precautions were taken to insure its purity, by successive crystallizations and fusions.

Two samples of copper were used, one from Lake Superior, the other from Germany. For the purification of the former, the sample was dissolved in sulphuric acid, with the addition of nitric acid; the solution was evaporated to dryness, and the solid heated over asbestos in a porcelain dish, until the fumes of sulphuric acid ceased coming off. The cupric sulphate was now dissolved in water, crystallized twice, and the diluted solution of the last crystals boiled and shaken with a little potassic hydrate for three hours. The solution was now filtered, and the cupric sulphate was crystallized several times from hot water. Finally, the solution of the last pure crystals, strongly acidified by sulphuric and a little nitric acid, was decomposed by the current of a Bunsen cell, and the chemically pure copper deposited on thick platinum foil.

The second example of copper was prepared from German cupric oxide in a similar manner, except that the sulphate was crystallized a greater number of times. In this connection it may be mentioned that, of many samples of German cupric oxide tested, not one was found which did not contain a comparatively large amount of arsenic. In the case of many samples, after several reductions with pure hydrogen and oxidations, the arsenic will actually sublime off as arsenious oxide; and a quantity of the substance was collected in this manner.

The method of cleaning the copper was similar to that previously adopted; it was treated in succession with dilute potassic hydrate, dilute sulphuric acid, and a very large amount of water, and then dried and reduced by pure hydrogen.

The silver which was obtained by precipitation from the pure argentic nitrate was first washed and dried at 150°, and weighed, as before; and was then heated to incipient redness, and weighed again. The loss of weight by this process varied with the different samples between three tenths of a milligram and one milligram. The Gooch crucible and asbestos mat subjected to the same treatment did not lose an appreciable quantity. The results were calculated for the weight of silver both before and after ignition, and it will be noticed that the first column of results corresponds almost exactly to the results given in the previous paper. The silver was in each case tested for copper, and no trace was found.

RESULTS.

GERMAN COPPER.

No. of Experiment.	Weight Cu.	Weight of Silver formed.		$Cu : Ag_2 = 1 : n$.	Atomic Weight Cu ($Ag = 107.675$).	
		Before Ignition.	After Ignition.		Before Ignition.	After Ignition.
	Grams.	Grams.	Grams.			
1	0.75760	2.5723	2.5713	3.3940	63.426	63.450
2	0.95040	3.2261	3.2256	3.3939	63.440	63.451
3	0.75993	2.5798	2.5794	3.3942	63.438	63.447
					Average,	63.449
Greatest variation = ±.002. Probable error = ±.0010.						

LAKE SUPERIOR COPPER.

No. of Experiment.	Weight Cu.	Weight Ag formed.		$Cu : Ag_2 = 1 : n$.	Atomic Weight Cu ($Ag = 107.675$).	
		Before Ignition.	After Ignition.		Before Ignition.	After Ignition.
	Grams.	Grams.	Grams.			
4	1.02060	3.4650	3.4640	3.3942	63.432	63.448
5	0.90460	3.0705	3.0701	3.3939	63.444	63.452
					Average,	63.450
Greatest variation = ±.002. Probable error = ±.0013.						

The average of these two series is 63.450, with greatest variations of +.002 and —.003, and a probable error of ±.0006. The average of the results calculated from the weight of silver dried at 150° is 63.436, while the results published in the preceding paper gave 63.437.

The complete concordance of these results with each other, and with the previous value above referred to, would point strongly to the following conclusions.

First, that the copper used in each case was absolutely free from metallic alloy; for manifestly the three entirely different samples would be likely to contain different impurities, or at least different amounts of the same impurity. The copper was tested for sulphur with the greatest care by solution in nitric acid and treatment with baric chloride, and no trace of cloudiness was perceptible. That the copper was *absolutely* free from impurity is not contended; only that it did not contain a weighable amount of impurity in one gram, the amount used in each experiment. It is manifest that attempts to purify the copper beyond this limit would be labor thrown away, and would produce no effect upon the atomic weight. For example, one tenth of a milligram is a very large amount of foreign material to suppose existing in a gram of copper purified with such care; but this large amount would only change the atomic weight five units in the third decimal place, — a quantity which is of no consequence when the atomic weight is in doubt three units in the first decimal place.

Another and still more positive conclusion reached by these results is that the atomic weight of copper is a constant quantity with reference to nitric acid and silver. If copper had a variable atomic weight, it would surely appear in specimens taken from such widely different sources. This conclusion still remains in force, even supposing there be a constant error in the process, for the constant error must affect all the results equally, and could not possibly equalize unlike results.

A third conclusion pointed out by the determinations is that the argentic nitrate was the normal compound, and quite pure; for it will be remembered that two entirely different samples had been used in the course of the work.

There is but one point which remains to be considered, and that is the existence or non-existence of a constant error in the reaction. That this is by far the most important point in the whole discussion, it is unnecessary to state. Whether there be such a constant error, future investigations may show; for the present, it is sufficient to say that it is extremely difficult to see where such an error might creep in. The whole reaction is so simple and so sharp, that the probability of error is reduced to a minimum, and in every case any possible cause of error has been guarded against.

Professor Cooke, under whose direction the whole investigation has been conducted, suggested that similar experiments be made, using argentic sulphate instead of the nitrate; but after a large number of trials this was found to be impracticable: first, because the solution has a much higher freezing point than that of the nitrate; and secondly, because the solution was necessarily so dilute, on account of the slight solubility of argentic sulphate, that the complete precipitation of the silver required a much longer time, giving more opportunity for secondary reactions. The silver was always accompanied by a very slight admixture of some basic cupric sulphate; and hence this method, which, if successful, would have been able to throw much light on the question of a constant error in the previous results, had to be abandoned.

CAMBRIDGE, December 15, 1887.